

ARMY RESEARCH LABORATORY



Liquid-Phase Sintering (LPS) of Tungsten-Based Heavy Alloys: Hafnium and Copper Addition

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13. ABSTRACT (Maximum 200 words) <p>Tungsten heavy alloys of composition 80W-20(Hf-Cu) weight-percent have been fabricated by liquid phase sintering (LPS). Two hafnium-rich, near eutectic compositions of the Hf-Cu system were utilized to lower the sintering temperature in the W-Hf system. Intermetallic compounds can be harmful to the mechanical properties of tungsten-based heavy alloys and avoiding them was deemed to be critical in the development of these new alloys. Therefore, an understanding of the processing conditions by which these compounds are formed was a vital component of this work. The threshold temperature for the formation of the intermetallic HfW₂ was determined by powder x-ray diffraction (XRD) to be ~1,400° C. This threshold temperature was well above the predicted LPS temperature of 1,310° C for hafnium-rich compositions in the Hf-Cu binary. To study the effects of cooling rates on the formation and stability of another possible intermetallic phase CuHf₂, uniaxially pressed 90Hf-10Cu elemental powder blends were heated to 1,310° C for 30 min and subjected to four different cooling rates. The CuHf₂ phase was, however, observed at room temperature for all cooling rates examined. Two ternary W-Hf-Cu compositions were selected by fixing the tungsten content at 80 weight-percent and utilizing two near eutectic Hf-Cu compositions. Copper additions in the W-Hf alloy system, however, resulted in the formation of the HfW₂ intermetallic phase at temperatures as low as 995° C. The microstructure was comprised of interpenetrating, semicontinuous networks of nearly pure W with HfW₂.</p>				
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TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENT	iii
LIST OF FIGURES	vii
LIST OF TABLES	vii
1. INTRODUCTION	1
2. EXPERIMENTAL PROCEDURE	2
3. RESULTS AND DISCUSSION	5
4. CONCLUSIONS	12
5. REFERENCES	13
DISTRIBUTION LIST	15

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LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Equilibrium binary-phase diagram of the (a) Hf-W and (b) Hf-Cu systems	3
2. XRD patterns of the 80W-20Hf weight-percent powder blends obtained at temperatures ranging from (a) 1,000° C to 1,300° C and (b) from 1,400° C and above	6
3. SEIs of the LPS binary 90Hf-10Cu weight-percent alloys obtained from the (a) FC and (b) WQ conditions	8
4. BEIs of the LPS 80W-17.7Hf-2.3Hf (weight-percent) alloys at 1,310° C obtained from an exposure time of (a) 60 min followed by a WQ, and (b) 5 min followed by an LNQ	10
5. BEI of the LPS 80W-13.7Hf-6.3Cu (weight-percent) alloy 3-K shows partially sintered W-Hf phase	11
6. BEI of the LPS 80W-13.7Hf-6.3Cu (weight-percent) alloy 3-0 cooled in a furnace shows microcracks	11

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. 80W-17.7Hf-Cu Alloy	9
2. 80W-13.7Hf-Cu Alloy	10

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1. INTRODUCTION

Classical tungsten heavy alloys (WHAs) are usually fabricated by liquid-phase sintering (LPS) of W-Ni-Fe or W-Ni-Cu elemental powder blends. These nickel-based heavy alloys have a two-phase composite structure of dispersed, nearly pure, tungsten grains embedded in a ternary alloy matrix. In recent years, extensive research has been performed with these heavy alloys to increase ballistic performance in kinetic energy (KE) projectile applications (Magness 1992; Baker and Dunn 1992; Noh et al. 1992; Magness 1994; Weerasooriya, Moy, and Dowding 1994; Guha et al. 1994). Although significant improvement has been made, the inability to form adiabatic shear localization bands in the WHAs during ballistic impact still limits the armor penetration depth and results in inferior performance, when compared to depleted uranium (DU) penetrators (Magness 1992). This barrier has led to the development of novel WHAs. The main approach has been the development of new matrix materials with their thermomechanical properties similar to those of DU (Baker and Dunn 1992; Magness 1994). It has been well established (Magness 1992, 1994; Magness and Farrand 1990) that the self-sharpening behavior of DU penetrators during ballistic impact is a competition between localized deformation hardening and localized thermal softening under extremely high hydrostatic pressure (~5–6 GPa). In order to induce thermomechanical instability prior to plastic deformation, an ideal matrix material would have low-heat capacity, low-thermal conductivity, low work-hardening rate, and low strain-rate hardening (Baker and Dunn 1992; Magness 1994). Because of the comparable thermal properties of hafnium as compared to those of DU, hafnium-based WHAs have indicated a propensity for thermal softening.

Magness (1995) has reported that W-Hf alloys have shown better ballistic performance than conventional WHAs in KE projectile applications. Recent work by Subhash, Pletka, and Ravichandran (1994) has indicated that polycrystalline hafnium has a high propensity for strain rate insensitive shear banding under uniaxial compressive loading. Although W-Hf alloys are shown to have potential for KE projectile applications, processing methods are limited due to the relatively high-liquidus ($>2,500^{\circ}\text{C}$) temperature (Rudy 1969; Spencer et al. 1981) for tungsten-rich compositions. This physical limitation makes LPS of W-Hf alloys impractical, and formation of the HfW_2 intermetallic is unavoidable. Subhash et al. (1994) have reported that hot-extruded, followed by multiple-swaged W-Hf alloys, have brittle fracture characteristics possibly due to the presence of HfW_2 . Ohriner, Sikka, and Kapoor (1994) have reported that W-Hf composites can be consolidated by hot extrusion. They also have reported HfW_2 formation at the $1,400^{\circ}\text{C}$ preheat temperature. Edelman, Pletka, and Subhash (1994) have reported that a W-Hf-Ti composite has been processed by mechanical alloying followed by vacuum sintering. Full

density has not been achieved at temperatures up to 1,450° C. All of the aforementioned novel processing techniques, however, have relatively high processing costs.

According to the Hf-Cu phase diagram (Spencer et al. 1981; Subramanian and Laughlin 1988), small additions of copper into the binary W-Hf system can substantially lower the LPS temperature. Since tungsten is insoluble in the liquid copper (Hansen and Anderko 1958), the W-Hf-Cu ternary system can be treated as a pseudo-binary alloy system. A constant tungsten content of 80 weight-percent was used in this study. This composition was consistent with the previous study by Magness (1995). He was able to observe that the 80W-20Hf (weight-percent) alloy resulted in improved ballistic performance as compared to conventional WHAs. Two near-eutectic, hafnium-rich Hf-Cu compositions are of particular interest in the present study. By inspection of the relevant binary-phase diagram, it was concluded that the formation of potentially harmful intermetallic phases could be avoided through proper processing. It was believed that the HfW_2 phase could be avoided by holding the processing temperature below some critical point where the reaction kinetics were sluggish enough to inhibit its formation. Concurrently, it was also required that the temperature be above the liquidus temperature of the binary Hf-Cu eutectic composition. This would provide a temperature window in which to process the ternary alloy. The process concept also recognized the necessity of avoiding the formation of the CuHf_2 intermetallic on cooling from the liquidus. Several cooling rates and media were investigated for the Hf-Cu binary to determine the optimum conditions. Binary 80W-20Hf (weight-percent) elemental powder blends were used to determine the threshold temperature for HfW_2 formation, and uniaxially pressed 90Hf-10Cu (weight-percent) elemental powder blends were used to determine the effects of the cooling rate on the formation of CuHf_2 from an LPS temperature of 1,310° C.

2. EXPERIMENTAL PROCEDURE

It has been well known that tungsten is insoluble in liquid copper in the binary W-Cu system (Hansen and Anderko 1958). Phase equilibria studies of ternary W-Cu-Al (Prevarskii and Kuzma 1983) and W-Cu-WSi₂ (Efimov et al. 1984) also reported negligible mutual solubility of copper and tungsten. Therefore, it is reasonable to assume that mutual solubility of copper and tungsten should be negligible in the ternary W-Hf-Cu system. In the equilibrium W-Hf binary system, as shown in Figure 1(a), solubility of hafnium decreases from ~9 weight-percent at ~2,512° C to ~4 weight-percent at ~1,400° C (Rudy 1969; Spencer et al. 1981). On the other hand, on the hafnium-rich side of the Hf-Cu binary system, a liquid phase begins to form at temperatures above 1,295° C (Spencer 1981; Subramanian and Laughlin 1988), as shown in Figure 1(b).

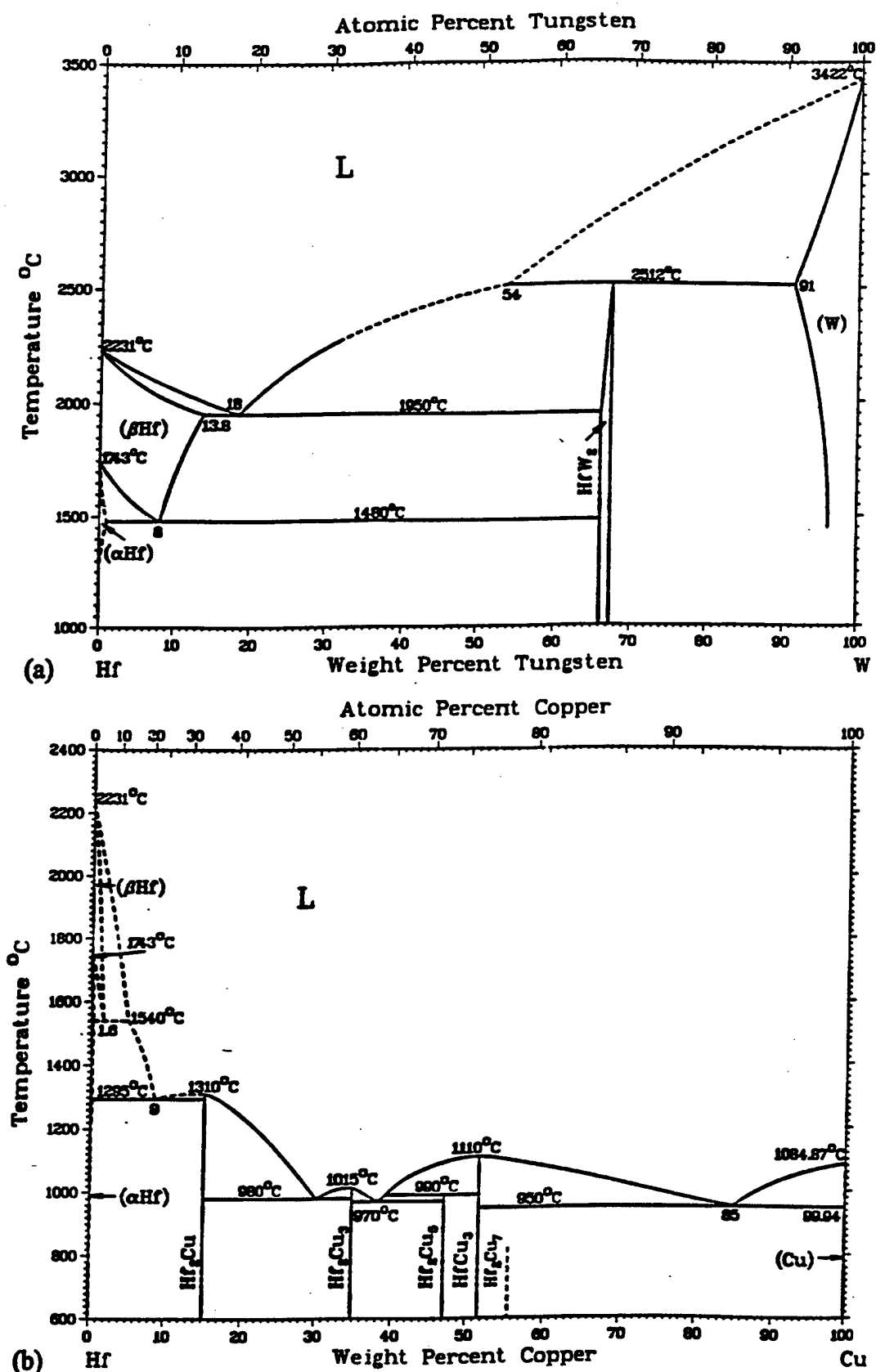


Figure 1. Equilibrium binary-phase diagram of the (a) Hf-W and (b) Hf-Cu systems (Spencer et al. [1981]).

The eutectic hafnium composition in the hafnium-rich Hf-Cu binary system is ~88.5 weight-percent (Subramanian and Laughlin 1988). Although the equilibrium-phase diagram predicts solubility of about ~3 weight-percent hafnium at ~1,300° C, the kinetics of reaction between tungsten and hafnium in the W-Hf-Cu systems are unknown. Initially, therefore, the ternary composition of 80W-20 (Hf-Cu) with a 88.5Hf:11.5 Cu ratio in weight-percent was selected. The main concern was how to avoid formation of two intermetallic phases in the W-Hf-Cu ternary system—namely, HfW_2 and CuHf_2 .

For determination of the threshold temperature for HfW_2 intermetallic formation, elemental powder blends of 80W-20Hf were prepared. Because of the potential pyrophoricity of hafnium elemental powders (-325 mesh), initial powder blends were prepared inside of a glove box filled with argon. Once tungsten and hafnium powders were placed in a container, subsequent mixing was done at ambient atmosphere. These powder blends were then placed on alumina crucibles and heated in a conventional tube furnace at temperatures ranging from 1,000° C to 1,500° C in increments of 100° C for 60 min. Additional exposure times of 240 and 480 min were investigated at 1,500° C. All experiments were done under ultra-high purity (grade 5) argon. All specimens were cooled to ambient temperature inside the furnace with a continuous flow of argon. Partially sintered powder blends were carefully ground and prepared for powder x-ray diffraction (XRD). Monochromated Cu $K_{\alpha 1}$ ($\lambda = 1.5406 \text{ \AA}$) radiation was utilized for qualitative HfW_2 intermetallic phase analysis using W(110) planes and HfW_2 (311) planes. All XRD data were obtained using a step-scan technique with increments of 0.02° and a counting time of 2 s per step. Radiation was generated using a 45 kV and 40 mA power setting.

Formation and stability of the CuHf_2 phase was examined using 90Hf-10Cu elemental powder blends. These powder blends were uniaxially pressed at a pressure of 165 MPa (~24 ksi) using a cylindrical-steel die. Disk-shaped specimens (29 mm diameter x 6 mm thickness) were placed in alumina crucibles and heated in a conventional tube furnace at a temperature of 1,310° C under ultra-high purity argon atmosphere. Four different cooling rates were selected to determine the formation CuHf_2 upon cooling from the liquidus temperature. To retain high-temperature phase(s) and microstructure, the specimen was water quenched (WQ). The equilibrium condition was simulated by furnace cooling (FC) the specimen with a continuous flow of argon. Two additional intermediate cooling rates were selected to examine the additional effects of phase formation. A specimen was cooled inside of the furnace with an increased argon flow rate of 10 times the rate used for sintering. This will be designated as the furnace fast-cooled condition (FCC). The last specimen was moved to an edge of the tube after the sintering and continuous flow of argon was applied by a high-speed nozzle blast. This condition will be designated as a nozzle-

quenched (NQ) condition. Specimens were sectioned using diamond wafering blades and mounted for optical and electron microscopy. CuHf_2 intermetallic phase was analyzed qualitatively using the XRD technique with monochromated $\text{Cu K}_{\alpha 1}$ radiation on the polished cross sections.

Based on the information obtained from the W-Hf and Hf-Cu binary systems, a processing window for W-Hf-Cu alloy was determined. Two near-eutectic compositions of the Hf-Cu binary system were utilized to lower the LPS temperature so that HfW_2 intermetallic-phase formation would be avoided. The selected ternary compositions were 80W-17.7Hf-Cu and 80W-13.7Hf-Cu (weight-percent), and their approximate LPS temperatures were determined to be 1,310° C and 995° C, respectively. These LPS temperatures were determined by using the Hf-Cu phase diagrams (Spencer et al. 1981; Subramanian and Laughlin 1988) since W is insoluble in the liquid copper (Hansen and Anderko 1958) and reactions between tungsten and hafnium are expected to be marginal in these temperature regimes (Rudy 1969; Spencer et al. 1981). For the 80W-17.7Hf-Cu alloy, the LPS temperature of 1,310° C was adequate. For the 80W-13.7Hf-Cu alloy, however, the initial sintering temperature of 995° C was too low to provide enough liquid phase to promote full sintering. Additional sintering temperatures of 1,025° C and 1,100° C were applied. Initial sintering times of 30 min and cooling conditions of FC, FCC, NQ, and WQ were selected. For the 80W-17.7Hf-Cu alloy, additional sintering times of 5 and 60 min and liquid nitrogen-quenched (LNQ) conditions were applied. All specimens were sectioned using diamond wafering blades for subsequent XRD analysis and metallographic examination.

3. RESULTS AND DISCUSSION

According to the XRD analysis of heat-treated elemental powder blends of W-Hf, the HfW_2 phase begins to form at ~1,400° C. This result is consistent with the observations by Subhash et al. (1994) and Ohriner, Sikka, and Kapoor (1994). Figure 2(a) shows results obtained in temperature ranges from 1,000° C to 1,300° C with an exposure time of 60 min. The interplanar spacing of W(110) and $\text{HfW}_2(311)$ are 2.238 and 2.272 Å, respectively (International Centre for Diffraction Data 1994). Corresponding diffraction angles, 2θ , are 40.24° and 39.64°, respectively. $\text{HfW}_2(311)$ peaks were not detected by XRD at 1,300° C and below. Figure 2(b) shows the results obtained at 1,400° C and 1,500° C with an exposure time of 60 min. Additional exposure times of 240 and 480 min were utilized to examine the kinetics of HfW_2 phase formation. The threshold temperature for HfW_2 phase formation was determined to be very close to 1,400° C. It should be pointed out that relative intensities shown in Figures 2(a) and 2(b) are magnified so that all the lines could be visible without overlapping. The amount

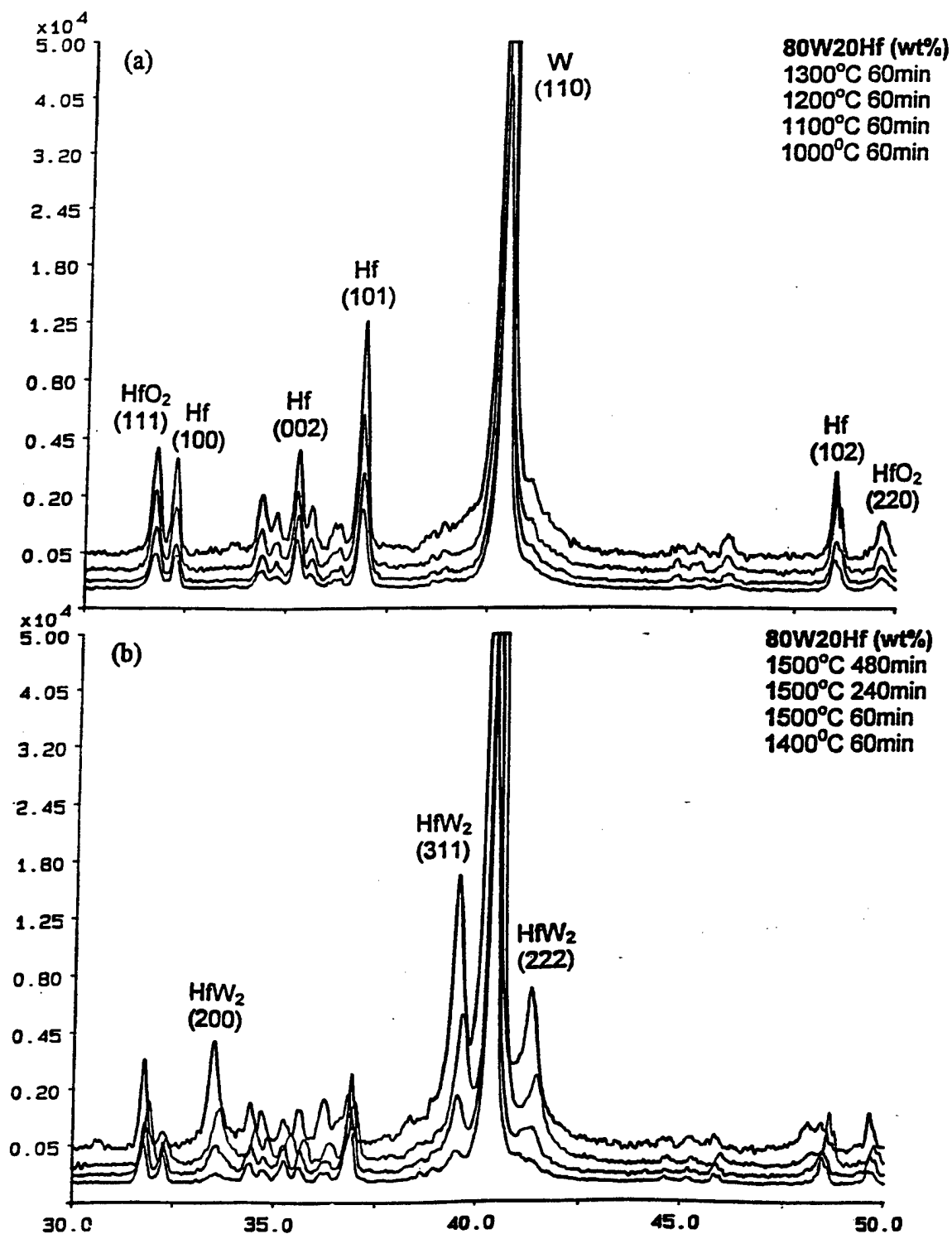


Figure 2. XRD patterns of the 80W-20Hf weight-percent powder blends obtained at temperatures ranging from (a) 1,000° C to 1,300° C and (b) from 1,400° C and above. At 1,400° C, HfW_2 phase formation is visible, see HfW_2 (311) plane.

of HfW_2 phase was increased with increasing temperature and increasing exposure time. The total amount of HfW_2 phase was determined to be less than 3 volume-percent even at a temperature of $1,500^\circ\text{C}$ with an exposure time of 480 min. This indicates that HfW_2 phase formation will be sluggish near or below $1,300^\circ\text{C}$.

The CuHf_2 phase has a body-centered tetragonal structure with lattice constants of $a = 3.1695$ and $c = 11.1333$ (Subramanian and Laughlin 1988; International Centre for Diffraction Data 1994). Hafnium has a hexagonal structure with lattice constants of $a = 3.1967$ and $c = 5.0578$ (International Centre for Diffraction Data 1994). Hafnium oxide (HfO_2) has two known monoclinic- and tetragonal-unit cell structures (International Centre for Diffraction Data 1994). Because of the similarities in the unit cell structures and resulting interfering peaks from hafnium and HfO_2 phases, qualitative phase analysis of CuHf_2 was difficult. There appeared to be, however, some trace amount of CuHf_2 phase (<3 volume-percent) from FC and FFC specimens. For the NQ specimen, however, the amount of HfO_2 phase increased significantly while diminishing the CuHf_2 phase, indicating selective consumption of available hafnium prior to formation of the CuHf_2 phase. For the WQ specimen, severe peak broadening was observed due to the lattice strain resulting from rapid cooling. It was also possible to have a nonstoichiometric compound. This deviation may cause a shifting of the interplanar spacing. This possibility made the quantitative phase analysis of CuHf_2 almost impossible. Although precise phase analysis was not possible, the amount of CuHf_2 phase seemed to be negligible enough in the W-Hf-Cu alloy system to proceed.

Figures 3(a) and 3(b) show secondary electron photomicrographs of the binary Hf-Cu alloy obtained from two of the four different cooling conditions. Scanning electron microscopy (SEM) analysis of the Hf-Cu alloy revealed a duplex composite structure of nearly pure Hf grains embedded in a Hf-Cu matrix. The microstructure was determined to be insensitive to the cooling conditions. The volume fraction of the Hf-Cu phase as seen in the SEM photomicrographs (Figure 3) was much more than the amount determined by the XRD analysis. The maximum solubility of copper in hafnium is only ~0.3 weight-percent at $1,540^\circ\text{C}$ and is decreased with decreasing temperature (Spencer et al. 1981; Subramanian and Laughlin 1988). At $1,310^\circ\text{C}$, therefore, solubility of copper in hafnium will be negligible. If, and only if, a nonstoichiometric Hf-Cu compound had formed, then hafnium-phase diffraction peaks will remain at the same 2θ location as pure hafnium peaks while shifting the Hf-Cu matrix-phase peaks in either direction. It is, therefore, possible to see complete overlapping diffracted peaks from hafnium and Hf-Cu

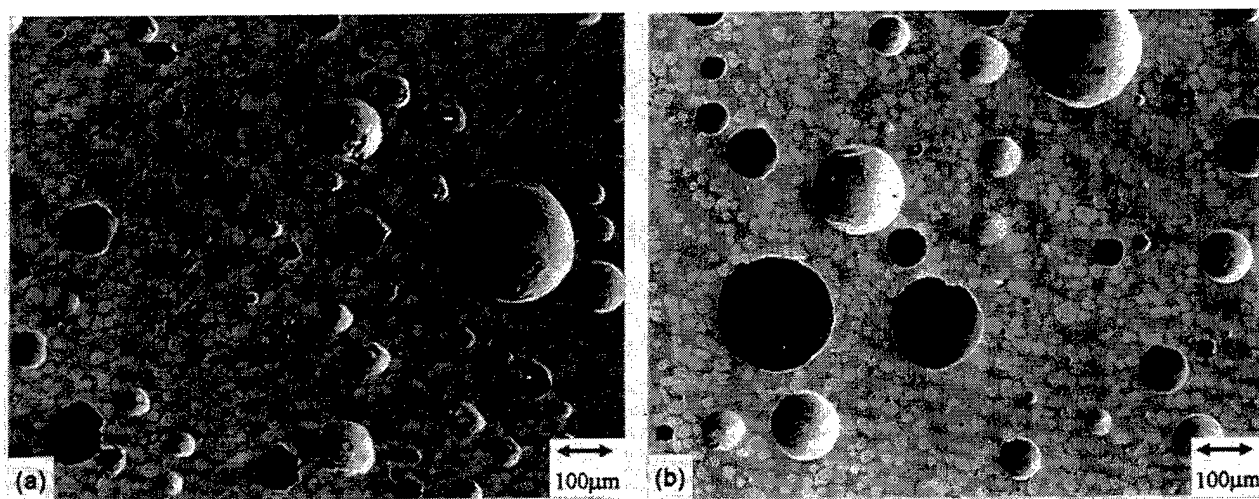


Figure 3. SEIs of the LPS binary 90Hf-10Cu weight-percent alloys obtained from the (a) FC and (b) WQ conditions.

matrix phases. On the other hand, zirconium always coexists with hafnium in nature. The hafnium powder utilized in the present study contains about 2.5 weight-percent zirconium according to the vendor (Teledyne Wah Chang Albany 1994). This residual zirconium may act as a third alloying element to form an unknown Hf-Cu-Zr compound. At the present time, however, the chemical and microstructural features of the Hf-Cu matrix phase have not been identified completely.

Two ternary W-Hf-Cu alloys (80W-17.7Hf-Cu and 80W-13.7Hf-Cu) were selected for LPS based on the information obtained from the two binary Hf-W and Hf-Cu systems. For the 80W-17.7Hf-Cu alloy, the LPS temperature was found to be 1,310° C, which was about 15° C above the liquidus temperature for the hafnium-rich side of the Hf-Cu binary eutectic composition (Spencer 1981; Subramanian and Laughlin 1988). Table 1 summarizes the data for cooling conditions, exposure time, and phases identified by XRD analysis. Surprisingly, HfW₂ intermetallic was identified in all cases, while the CuHf₂ phase was not detected by XRD. An additional attempt to increase the cooling rate was made in order to avoid formation of the HfW₂ phase by using liquid nitrogen as a quench media. However, the HfW₂ phase was still present in the LNQ specimen.

At the present time, only alloys 3-D to 3-G have been examined by SEM and energy dispersive x-ray spectroscopy (EDXS). Thus far, there has been no indication of the presence of the CuHf₂ phase.

Table 1. 80W-17.7Hf-Cu Alloy

Alloy ID	LPS Temp (°C)	Time (min)	Cooling	Sintered	Phases by XRD
3-A	1,310	30	FC	Yes	W+HfW ₂
3-B	1,310	30	FFC	Yes	W+HfW ₂
3-C	1,310	30	NQ	Yes	W+HfW ₂
3-D	1,310	30	WQ	Yes	W+HfW ₂
3-E	1,310	60	WQ	Yes	W+HfW ₂
3-F	1,310	5	WQ	Yes	W+HfW ₂
3-G	1,310	5	LNQ	Yes	W+HfW ₂

Note: All specimens had a minor HfO₂ phase.

Microstructures of the rapidly cooled specimens did not result in the duplex composite structure of classical WHAs typically characterized by well-defined tungsten grains. Instead, semicontinuous networks of tungsten grains dispersed in a HfW₂ matrix phase were seen. According to the limited EDSX analysis, copper was not detected at or near the HfW₂ phase. The occasional appearance of copper was always accompanied by the tungsten phase. Therefore, it is speculated that dispersed copper may act as a heterogeneous nucleation site for HfW₂ intermetallic formation rather than reacting with tungsten and hafnium to form a W-Hf-Cu compound. The microstructure was insensitive to the exposure time as seen in Figures 4(a) and 4(b), which show backscattered electron images (BEIs) of alloys 3-E and 3-G, respectively. LNQ specimens showed excess quench cracks resulting from the rapid cooling. EDSX analysis of the cracked area indicates that in every case pure tungsten phase is responsible for the cracking. Oxygen was also detected from the cracked area.

For 80W-13.7Hf-Cu alloys, an initial LPS temperature of 995° C was selected. After an exposure time of 30 min, full sintering was not possible. Therefore, two additional sintering temperatures of 1,025° C and 1,100° C were applied. Full sintering was obtained at 1,100° C. Table 2 summarizes the results obtained from the LPS experimentation. It appears that the formation of a liquid phase is initiated by the melting of Cu followed by the formation of the liquid Hf-Cu phase. Therefore, at LPS temperatures above the melting temperature of copper (1,083° C), liquid-phase formation would be accelerated, which in turn results in decreasing sintering time. Figure 5, BEI of the alloy 3-K which was WQ from 995° C, shows such a trend. The nearly pure copper phase with a trace of tungsten (identified

Table 2. 80W-13.7Hf-Cu Alloy

Alloy ID	LPS Temp (°C)	Time (min)	Cooling	Sintered	Phases by XRD
3-H	995	30	FC	No ^a	W+HfW ₂ +Cu
3-I	995	30	FFC	No ^a	W+HfW ₂ +Cu
3-J	995	30	NQ	No ^a	W+HfW ₂ +Cu
3-K	995	30	WQ	No ^a	W+HfW ₂ +Cu
3-M	1,025	30	NQ	No ^a	W+HfW ₂ +Cu
3-N	1,025	30	WQ	No ^a	W+HfW ₂ +Cu
3-O	1,100	30	FC	Yes	W+HfW ₂
3-P	1,100	30	FFC	Yes	W+HfW ₂
3-Q	1,100	30	NQ	Yes	W+HfW ₂
3-R	1,100	30	WQ	Yes	W+HfW ₂

All specimens had a minor HfO₂ phase.

^aPartially sintered.

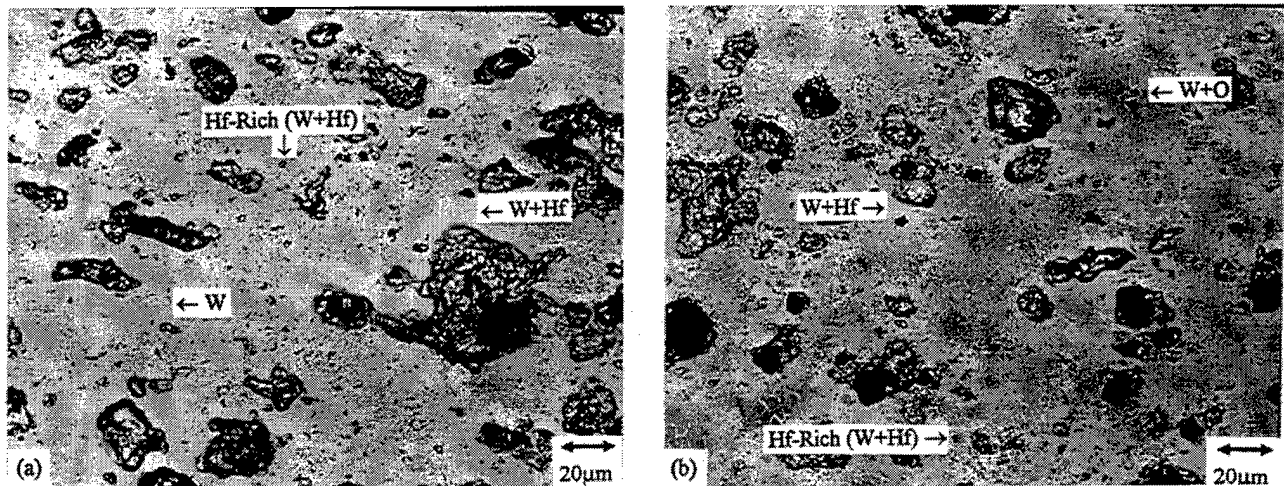


Figure 4. BEIs of the LPS 80W-17.7Hf-2.3Hf (weight-percent) alloys at 1,310° C obtained from an exposure time of (a) 60 min followed by a WQ and (b) 5 min followed by an LNQ.

as Cu+W in Figure 5) is surrounded by the tungsten-matrix phase. The mixture of W-Hf-Cu phase(s) (identified as W+Hf+Cu in Figure 5) is also surrounded by the tungsten-rich W-Cu phase (gray portion of the area identified as W+Cu) and the copper-rich W-Cu phase (white portion of the area identified as W+Cu). The copper phase was identified by XRD analysis in all partially sintered specimens. For fully sintered specimens, however, the copper phase was not detected by XRD analysis. It is not clear if the CuHf_2 phase is present in the W-Hf-Cu alloy system.

Thus far, SEM and EDSX analyses have been completed only for alloys 3-H, 3-K, 3-O, and 3-P. As evidenced in Figure 5, substantial microcracks resulted from the water quench. According to the EDSX analysis, mainly W and residual copper and oxygen were present in the cracked area. Specimen 3-O showed occasional microcracking, while specimen 3-P, which cooled much faster, showed none. Figure 6 shows BEI of the alloy 3-O illustrating microcracked areas consisting of mainly pure tungsten phase with a trace of copper, Hf-Cu phase, and a HfW_2 matrix phase with a trace of copper. It is not clear whether excess oxidation of the tungsten phase was responsible for such microcracking. It is also possible that liquid copper surrounding the tungsten grains reacts with oxygen and forms a spinel-type compound at the grain boundaries. There was no evidence of cracking at or near the grain boundaries between the tungsten and HfW_2 phases, or within the HfW_2 phase.

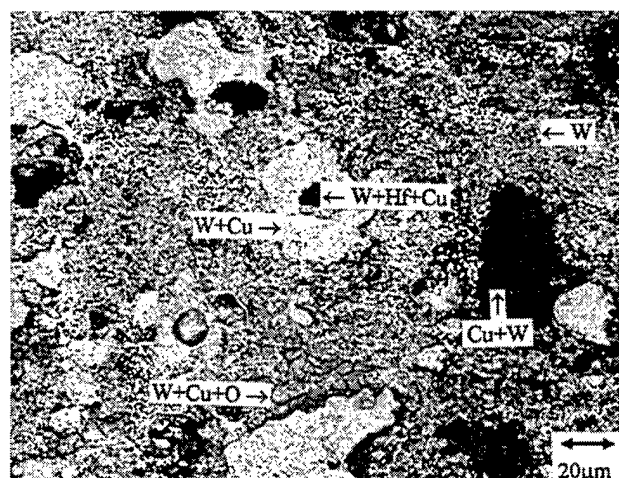


Figure 5. BEI of the LPS 80W-13.7Hf-6.3Cu (weight-percent) alloy 3-K shows partially sintered W-Hf phase.

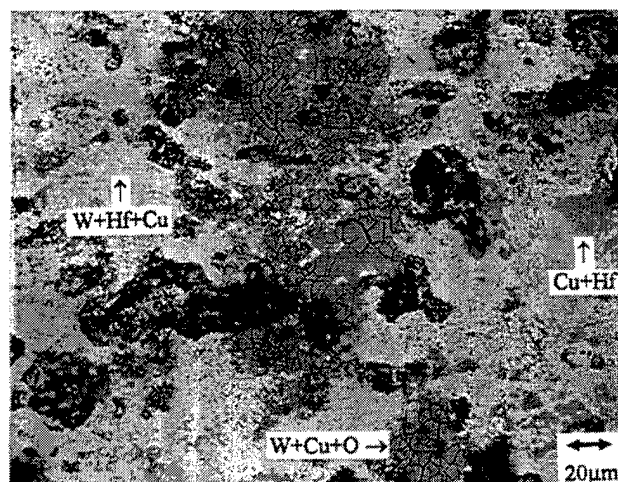


Figure 6. BEI of the LPS 80W-13.7Hf-6.3Cu (weight-percent) alloy 3-O cooled in a furnace shows microcracks.

4. CONCLUSIONS

The following preliminary conclusions were made based on the initial investigation of two W-Hf-Cu alloy systems.

- 80W-17.7Hf-Cu and 80W-13.7Hf-Cu alloys were LPS at temperatures of 1,310° C and 1,100° C, respectively.
- The threshold temperature of the HfW_2 phase formation in 90W-Hf binary system was about 1,400° C.
- HfW_2 phase was detected in the ternary W-Hf-Cu LPS alloy at temperatures as low as 995° C.
- Cu additions seem to accelerate and stabilize the HfW_2 phase formation.
- CuHf_2 phase was not suppressed by a rapid quench from 1,310° C in the 90Hf-10Cu binary system.
- Formation of the HfW_2 phase in the ternary system was insensitive to the cooling rates examined.
- A duplex composite microstructure of the classical WHAs was not observed in the rapidly cooled ternary LPS alloys. Instead, a semicontinuous network of tungsten grains in an HfW_2 matrix phase was obtained.
- Trace Cu was observed in the presence of W, and also with the W and Hf in the low and high Cu-content alloys, respectively. No evidence of the CuHf_2 phase, however, was found.

The authors would like to emphasize that these conclusions are still preliminary and based on the limited data obtained at the present time.

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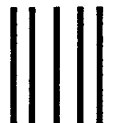
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